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Measurement of static electric dipole polarizabilities of lithium clusters: Consistency with measured dynamic polarizabilities

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Static electric dipole polarizabilities of lithium clusters made of n ($n=2-22$) atoms have been measured. The experiment consists of deflecting a collimated cluster beam through a static inhomogeneous electric field. The strong decrease per atom from Li to Li_3-Li_4 shows that electronic delocalization is reached for very small sizes. Moreover, directly measured polarizabilities are consistent with photoabsorption data. They thus confirm unambiguously the ''missing'' optical strength in lithium clusters. [S1050-2947(99)50301-6]

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The static electric dipole polarizability, α_0, is a basic observable for discussing electronic properties of clusters made of alkali-metal atoms, since it is very sensitive to the effectiveness of the delocalization of valence electrons, as well as to the structure and shape. For a review of polarizability physics, see Ref. [1], and for a review of metal clusters, see Ref. [2]. Despite numerous investigations of alkali-metal clusters, polarizability measurements are only available for sodium clusters and for selected sizes of potassium clusters [3], while nothing is known about lithium clusters. However, the static and dynamic response of lithium clusters to electric fields is, in many respects, the most interesting and puzzling. In the bulk limit, the static electric polarizability of a perfectly conducting sphere of radius R is given by $\alpha_{\mathrm{cl}}=R^3$. The polarizabilities of lithium and sodium atoms are very similar ($\alpha_{\mathrm{Li}}=24.4\,\text{Å}^3$, $\alpha_{\mathrm{Na}}=23.6\,\text{Å}^3$), while the classical values for the corresponding metallic spheres ($\alpha_{\mathrm{cl}}=r_s^3N$) are very different, since the Wigner-Seitz radii r_s at the melting temperature are 1.75 Å and 2.15 Å for Li and Na, respectively. Considering the atomic polarizability on the one hand, and the bulk limit value on the other hand, experimental data are needed to determine whether the response of a lithium cluster to a static electrical field corresponds to the expected one for a finite metallic sphere or keeps the memory of the abnormally large atomic value.

Furthermore, the dipole resonance of lithium clusters measured in photoabsorption spectra [4,5] is significantly redshifted as compared either to the prediction of the Mie theory [$\omega_M^2=4\pi e^2\rho/(3m)$, where ρ is the density of atoms in the sphere], or to the jellium model, which assumes a complete delocalization of valence electrons and neglects the underlying ionic structure (for reviews, see Refs. [6,7]). On the other hand, these approaches predict reasonably well the frequencies of the resonances observed for sodium and potassium clusters. The lithium shift has been traced to nonlocal effects in the electron-ion interaction that invalidate the simple jellium approach [8–10]. For a metallic sphere, the Mie frequency is directly related to the polarizability of the sphere,

$$\omega_M^2=\frac{e^2N}{m\alpha_{\mathrm{cl}}}. \tag{1}$$

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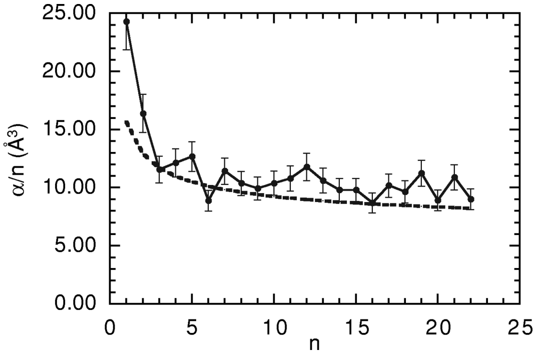

FIG. 1. Static dipole polarizability per atom (Å^3) of lithium clusters as a function of the number of atoms in the cluster. The dashed line represents the prediction from the classical metallic sphere [Eq. (3)], assuming a radius of 1.75 Å , and an electron spillout of 0.75 Å.

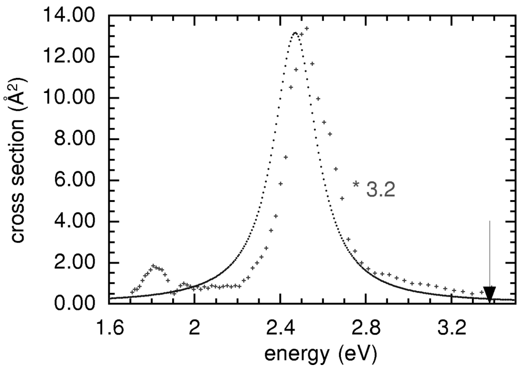

FIG. 2. Comparison of experimental photoabsorption cross section (Å^2) of Li$_8$ (solid line) and calculated transition (dashed line). The experimental data are from Ref. [4]. The experimental curve has been scaled to the theoretical values by a factor of 3.2 (experimental absolute values are hard to obtain). Every calculated transition has been broadened with a 0.25-eV-width Lorentzian. The Mie resonance of the corresponding metallic sphere is at 3.37 eV (vertical arrow).

A direct experimental determination of the electric polarizability is therefore crucial both for understanding the size evolution and for the interpretation of the optical response. In this Rapid Communication we present a measurement of lithium cluster polarizabilities and compare the results with theoretical calculations and experimental photoabsorption cross sections.

Briefly, the polarizability measurements are made by deflecting a well-collimated beam through a static inhomogeneous transverse electric field. Lithium clusters are produced in a supersonic beam. Lithium vapor (0.1 bar pressure) is coexpanded with argon (3 bars pressure) through an aperture of 100 μm in diameter. The collinear part of the beam is extracted by a skimmer and collimated by two 0.4-mm slits. The distance between the two slits is 1 m. The beam passes along the axis between the two cylindrical pole faces of a 15-cm-long deflector. A difference of potential of 30 kV can be applied between the two pole pieces, which are 1.7 mm apart. With the electric-field magnitude along the z axis denoted by E, the force acting on the passing cluster is

$$F_z = \alpha E \frac{dE}{dz}. \tag{2}$$

Outgoing clusters are ionized by a low flux laser ($\lambda = 308$ nm or $\lambda = 266$ nm) at a distance of 1 m out of the deflector, and are subsequently mass selected in a time-of-flight (TOF) mass spectrometer. We have checked carefully that no multiphotonic effect took place for the laser powers that we used. The set of voltages applied in the TOF mass spectrometer is adjusted so that the arrival time on the detector is sensitive to the ionization position. The polarizability is proportional to the measured deflection in the z direction: $\Delta z = KF_z/(Mv^2)$, where M is the mass of the cluster and v is the velocity. The constant K is a geometrical factor that actually does not need to be precisely known, since it cancels (along with E) when one takes the ratio of the polarizability of a given cluster and the well-known polarizability of the sodium atom. The velocity is determined by means of a coaxial TOF measurement. In this TOF measurement, after being ionized and before being accelerated and mass selected, clusters fly along a 2-cm-long path free of electric field. The precision of the measured polarizabilities is estimated to be at most 10%, in which the main source of error is the velocity measurement. The relative precision between clusters with neighboring masses is better. In order to avoid any systematic error, measurements of sodium cluster polarizabilities were also carried out. The values we have obtained are in close agreement with previous measurements [3].

TABLE I. Static dipole polarizability per atom (Å^3) of free lithium clusters. Experimental errors are in the range of 10%.

n	Experiment	*n*	Experiment	*n*	Experiment
2	16.4	9	9.9	16	8.7
3	11.5	10	10.4	17	10.2
4	12.1	11	10.8	18	9.6
5	12.7	12	11.8	19	11.2
6	8.9	13	10.6	20	8.9
7	11.4	14	9.8	21	10.9
8	10.4	15	9.8	22	9.0

Figure 1 shows the absolute static polarizability (per atom) for lithium clusters. The values are listed in Table I. The values measured for the atom and for the dimer (24.3 Å^3 and 32.8 Å^3, respectively) are in agreement with the published data (24.3 Å^3 [11] and 34.0 Å^3 [12,13], respectively). One observes a sharp decrease in the polarizability per atom by about a factor of 2 from the monomer to the trimer. For larger sizes, $n \geqslant 4$, the polarizability per atom is slowly decreasing. Small oscillations are superimposed on the average trend, especially for $n \geqslant 15$, where one observes a marked odd-even alternation. The classical polarizability, modified for the spillout of electrons from the surface of a nanometric metallic sphere, is given by

$$\alpha = (N^{1/3} r_s + \delta)^3, \tag{3}$$

where r_s is the Wigner-Seitz radius (1.75 Å) and δ is the electronic spillout (0.75 Å) [4]. The modified classical polarizability is also plotted in Fig. 1. The experimental values for $n \geqslant 4$, although globally higher, are relatively close to the calculated ones. Both the sudden transition from atom to trimer and the following slow variation suggest that the electronic delocalization already appears for sizes as small as 4 or 5. This is supported by the fact that the plasmon resonance appears in the same size range in lithium clusters [4]. We note however that the latter is clearly observed only for sizes larger than 6, while the static response tends to indicate that electronic delocalization is achieved at a smaller size. This quantitative difference is consistent with the fact that the optical absorption is very sensitive to the details of the electronic ditribution, and thus the geometry of the cluster, while the polarizability is essentially sensitive to average electronic properties.

Both the sharp decrease in the polarizability and the appearance of the plasmon resonance are signatures of the delocalization of valence electrons. However, as mentioned in the introduction, the dynamic response is strongly redshifted as compared to the resonance calculated for the metallic sphere. Figure 2 shows the optical photoabsorption spectrum of Li_8 clusters, measured some years ago [4]. The spectrum is dominated by a strong resonance at about 2.5 eV, just as in Na_8 clusters [14,15], though the density of lithium is larger than the density of sodium by about 80%. This immediately rules out a simple interpretation of the observed resonance in Li_8 in terms of the simple jellium model, which works well for sodium clusters. The latter will naturally predict the dipole resonance in Li_8 to lie above that of Na_8 by about 35%, i.e., around 3.4 eV (indicated by the arrow in Fig. 2). Such a strong redshift of the experimental resonance, with respect to the jellium model prediction, has also been systematically observed in charged lithium clusters [5,16].

For a thorough understanding of the electronic properties of lithium clusters, we compare both the static and dynamic responses with the prediction of pseudopotential calculations. The shift in the absorption spectrum is now well understood, and is due to nonlocal electron-ion interactions. Since lithium has only *s* core electrons, *s*-wave delocalized electrons cannot scatter deep in the core region due to Pauli repulsion, whereas *p*-wave electrons do not suffer such a repulsion. This means that a physically sound pseudopotential for lithium should have an $l=0$ component different from the $l\neq 0$ components. Note that for sodium, which has *s* and *p* core electrons, nonlocal effects are expected to be much weaker. A thorough analysis of nonlocal electron-ion potential effects in lithium clusters has been carried out in Ref. [9], where all the details can be found. Briefly, the dynamical polarizability is worked out in the random-phase approximation with exact exchange (RPAE), applied to the valence electrons moving in an external nonlocal potential. The latter is built as a convolution of the ion distribution with the nonlocal electron-ion pseudopotential. Only clusters with closed shells (8, 20, . . .) are considered here. Nonlocal effects lead to two dramatic consequences for the distribution of dipole oscillator strength. The first is a substantial redshift of the giant dipole resonance. In the case of Li_8, the theory actually yields a single optical transition at 2.47 eV, in perfect agreement with the mean position of the experimental resonance [4]. The calculated theoretical displacement may be phenomenologically understood in terms of effective mass. Allowing for nonlocal effects in the electron-ion interaction, the Mie frequency ω_M should be replaced phenomenologically by $\omega=\omega_M/\sqrt{m^*/m}$, where m^* is an effective electronic mass. The effective mass for bulk lithium is of order $m^*\simeq 1.4m$ [9].

TABLE II. Measured static dipole polarizability (Å^3) of closed-shell lithium clusters of size *n* (Expt.), compared to different theoretical estimates (*T*).

n	Expt.	*T* (this work)	*T* [10]	*T* [4]	*T* [17,18]
8	82.4	84.7	78.6	99.2	97
20	178.2	171.1	160.8		

The second effect of the nonlocality is a violation of the Thomas-Reiche-Kuhn sum rule. This time-honored sum rule ensures that the total sum of oscillator strength is exactly given by the number of valence electrons, but the rule only holds when the Hamiltonian is local, which is the case in the normal jellium model. Approximating the nonlocality with a constant effective mass m^*, the dipole sum rule is multiplied by the ratio m/m^* such that the effective number of active electrons is $N^{\mathrm{eff}}\simeq 0.77N$ in lithium clusters. The ''missing'' strength is to be found in the high-energy part of the spectrum, i.e., in the energy scale of core-electron excitations. It is worth noting that already in the lithium atom, the $2s\text{-}np\ (n\geqslant 2)$ transition accounts only for 75% of the oscillator strength, whereas for sodium, the $3s\text{-}np\ (n\geqslant 3)$ transition accounts for almost all of the oscillator strength. The static dipole polarizability is related to the dipole oscillator strength distribution, through the second-order perturbation theory expression,

$$\alpha_0=\frac{e^2}{m}\Sigma_k\frac{f_k}{\omega_k^2}, \tag{4}$$

where *m* is the electron mass and ω_k is the transition frequency from the ground state to the dipole state *k* with associated dipole strength f_k. Let us assume that the optical strength is concentrated into a single collective resonance. According to Eq. (4), the electric dipole polarizability can then be written as

$$\alpha_0=\frac{e^2N^{\mathrm{eff}}}{m\omega^2}, \tag{5}$$

where N^{eff} is the reduced strength and ω is the calculated resonance frequency $[\omega^2=\omega_M^2(m/m^*)]$. One can see that, within the present approximations (single transition, m^* constant, . . .), the nonlocal effects in Eq. (5), acting on both the oscillator strength and the frequency, cancel out. This explains why experimental polarizabilities are in close agreement with those of the finite metallic sphere. It is also in agreement with the classical limit, where the static polarizability depends only on the metallic volume and not on the effective mass of the electron.

Let us now make a more quantitative comparison between theoretical predictions and experimental polarizabilities (see Table II). Using Eq. (4) and the calculated oscillator strength distributions of Ref. [9], we estimate the theoretical dipole polarizability of Li_8 to be 84.7 Å^3, in good agreement with the experimental value of 82.9 Å^3, and that of Li_{20} to be 171.1 Å^3, also in fair agreement with the experimental value of 178.2 Å^3. A similar agreement is observed with recently reported calculations of the static and dynamic polarizability of lithium clusters, performed within the framework of the time-dependent local-density approximation, and also using nonlocal pseudopotentials [10]. According to the latter work, the static dipole polarizabilities of Li_8 and Li_{20} are 78.6 Å^3 and 160.8 Å^3, respectively. Moreover, in agreement with the above discussion, in the calculation of Ref. [10], the local reduction of the pseudopotential to the *s* component strongly affects the position of the optical resonance, while it does not modify the calculated static polarizability. Finally, it is interesting to remark that the *ab initio* calculations of Refs. [4] and [17] accurately predict the dynamic response of Li_8, but overestimate the static response. Note that we guessed that the theoretical value of 33 Å^3, reported in Ref. [17], had to be multiplied by a factor of 3 (this error was indeed confirmed by the authors, who gave us a value of 97 Å^3 [18]). These two calculations do not yield the same equilibrium geometry, but one does not expect the static polarizability to depend strongly on the exact geometry for a roughly spherical system with delocalized electrons.

To conclude, we provide direct measurements of static electric dipole polarizabilities of free lithium clusters, Li_n $(n=1-22)$, using a beam deflection method. The strong decrease of the polarizability per atom from $n=1$ to $n=3$, followed by a weak average size variation, reveals that the electronic delocalization is already reached for a size as small as $n=4$. The measured polarizabilities agree nicely with our theoretical predictions. The agreement for static and dynamic response can be reached only when one explicitly treats the nonlocality in the electron-ion pseudopotential in order to account for the important difference between *s* and *p* scattering, as the ion core has only *s* electrons. Measured static dipole polarizabilities are thus consistent with measured dipole resonance frequencies. They provide indirect but strong evidence that a fraction of the dipole strength has been removed from the optical region into higher frequencies. Our calculation explains why the effective mass due to nonlocality strongly affects the dynamic response but has little effect on the static response, which is close to the response of a finite metallic sphere with fully delocalized electrons.

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